Migratory Aptitudes in the Elimination-Rearrangement Reactions of 1,1-Diaryl-2-Bromoethylenes

By

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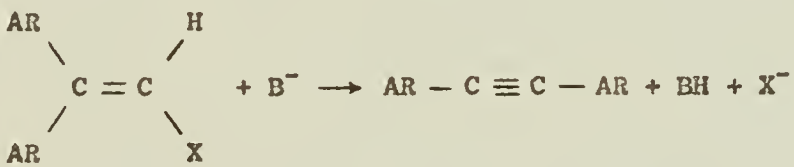
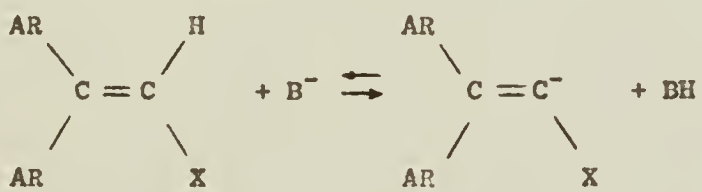
CHAPTER I

INTRODUCTION

The elimination and rearrangement reactions of 1,1-diaryl-2-haloethylenes with strong bases to yield diarylacetylenes (tolans) was first reported by Fritsch [1], Buttenberg [2], and Wiechell [3].

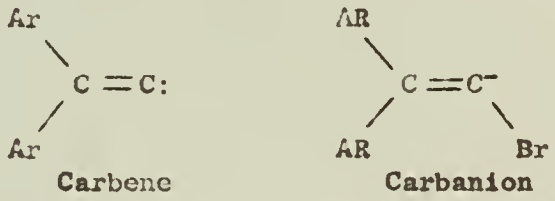


They used ethanolic solutions of sodium ethoxide at 180-200° to promote reactions. More recently, potassium amide in liquid ammonia [4,5] butyl- and phenyl-lithium in ether [6,7] and potassium-t-butoxide in t-butyl alcohol [8,9] have been used to produce high yields of tolans. Due to the general base initiation, the first step in the reaction is believed to be the abstraction of a proton to form the diaryl vinyl anion.



Curtin and Flynn [7] have proposed this to be the rate determining step in their system in which they used butyl-lithium as the base, while Pritchard and Bothner-By [9] have shown it to be a rapid equilibrium reaction under their conditions with potassium-t-butoxide.

The rearrangement step has been shown to be stereospecific. In the reaction of cis- and trans-1-p-bromophenyl-1-phenyl-2-bromoethylene with potassium-t-butoxide, the group trans to the leaving bromide ion migrates preferentially [8]. Cis- and trans-1-p-chlorophenyl-1-phenyl-2-bromoethylene rearranges similarly when promoted by butyllithium [10]. These results exclude the possibility of a carbene being involved in the major reaction and strongly suggest a geometrically stable vinyl carbanion as an intermediate in the reaction.



The effect of the leaving halogen on the rate of the reaction is known [8]. The purpose of our work was to make a kinetic study of the migratory aptitudes of phenyls containing various substituents. For this purpose the cis and trans isomers of 1-p-methoxyphenyl-1-phenyl-2-bromoethylene (cis- and trans-I), 1-p-chlorophenyl-1-phenyl-2-bromoethylene (cis- and trans-II) and 1,1-diphenyl-2-bromoethylene (III) were prepared. Dipole moment studies were also undertaken to determine the configurations of the high and low melting isomers of 1-p-methoxyphenyl-1-phenyl-2-bromoethylene.

Potassium-t-butoxide-t-butyl alcohol was chosen as our reaction medium for several reasons. Proton transfer is known to be a rapid step under these conditions [9] leading to the presumption that substituted phenyl groups will change the rate of the reaction as

compared to phenyl groups. Few, if any, side reactions occur with this base and relatively simple analysis of products can be obtained.

CHAPTER II

EXPERIMENTAL

A. Syntheses and Reactions

1-p-Methoxyphenyl-1-phenylethylene

This compound was prepared by adapting the method used by Nielson and McEwen [11] in the preparation of a similar compound. Twenty-four grams (1 mole) of magnesium was placed in a three-necked one-liter flask equipped with a reflux condenser and a stirrer. Seventy-eight grams (0.5 mole) of dry, freshly distilled bromobenzene in 200 ml. of dry ether was added dropwise over a two-hour period. The reaction started with stirring after a few milliliters of bromobenzene had been added. The reaction mixture was then refluxed for one hour, cooled, and 50 g. (0.32 mole) of p-methoxyacetophenone in 50 ml. of dry ether added over one hour. After refluxing for one hour the reaction mixture was hydrolyzed with 30 g. (0.565 mole) of ammonium chloride in 60 ml. of water. The organic and aqueous layers were separated and the aqueous layer extracted with ether. The organic layers were combined. The ether was removed by distillation and 100 ml. of 20 percent sulfuric acid was added to the cooled mixture. After refluxing for one hour the organic layer was separated. Yellow crystals appeared upon cooling the organic layer. Recrystallization from 95 percent ethanol* gave 40.8 g. (0.178 mole,

*Ninety-five percent ethanol will be called ethanol in this text.

55.5 percent) of white crystals, melting point* 74-76° (lit. [12] 75°). Repeating this experiment under essentially the same conditions afforded a yield of 53 percent.

cis- and trans-1-p-Methoxyphenyl-1-phenyl-2-bromoethylene (cis- and trans-I)

Thirteen grams (0.064 mole) of 1-p-methoxyphenyl-1-phenylethylene was brominated with 10.5 g. (0.065 mole) of bromine in 50 ml. of carbon disulfide. The addition took forty-five minutes and was allowed to reflux with no aid. Hydrogen bromide was liberated after about 20 ml. of the bromine solution had been added. The mixture was then refluxed overnight. Carbon disulfide was removed by distillation and the residual oil dissolved in ethanol. White crystalline needles were obtained upon cooling. These were removed and the solution set aside for one week, during which time more crystals came out of solution. A total of 4.45 g. (0.015 mole, 23.4 percent) of the trans** isomer was obtained. These were recrystallized from ethanol, m.p. 81-82° (lit [12] 82.5°)

The resultant filtrate, from which the trans isomer had been removed, was passed through a 1 x 30 cm. column of alumina eluting with ethanol. Twenty milliliter samples were collected and allowed to evaporate at room temperature. Yellow oil and white crystalline flakes came out of solution and were separated by filtering.

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*All melting points and boiling points are uncorrected.

**The trans configuration was assigned by Stoermer and Simon 12 and confirmed by dipole moment measurement (see discussion) by the author.

Recrystallizing the white crystals from ethanol gave 1.05 g. (0.0036 mole, 5.5 percent) of cis isomer, m.p. 55-56° (lit. [12] 52°).

1,1-Diphenylethylene

1,1-diphenylethylene was prepared according to the method of Allen and Converse [13].

1,1-Diphenyl-2-bromoethylene

The bromination of 1,1-diphenylethylene was performed using the procedure of E. Hepp [14].

The product was recrystallized from methanol to yield very white crystalline flakes, m.p. 42-43° (lit. [14] 40°).

1-p-Chlorophenyl-1-phenylethylene

This compound was prepared using a modification of Curtin's [10] procedure. Seventy-two grams (3 moles) of magnesium was placed in a dry two-liter three-necked flask. Approximately 143 g. (1.5 moles) of methyl bromide in 500 ml. of dry ether was added over three hours. The reaction was allowed to reflux without external heating. At the end of this time an ether suspension of 150 g. (0.695 mole) of p-chlorobenzophenone was added in small portions. The reaction was refluxed for two hours and then hydrolyzed with 53.5 g. (1 mole) of ammonium chloride in 200 ml. of water. After separating the layers and washing the organic layer with water, the ether was removed by distillation and the resultant carbinol was dehydrated with 200 ml. of 20 percent sulfuric acid. After separating the organic

and aqueous layers the organic layer was dried and the remaining oil fractionated under reduced pressure through a 6-in. column packed with glass helicies. One hundred grams (0.45 mole, 66.5 percent) of 1-p-chlorophenyl-1-phenylethylene, b.p. 151-158° (5-8mm.) lit. [10] b.p. 153-158° (10 mm.), was obtained.

cis- and trans-1-p-Chlorophenyl-1-phenyl-2-bromoethylene (cis- and trans-II)

Fifty grams (0.232 mole) of 1-p-chlorophenyl-1-phenyl-ethylene was brominated with 44.2 g. (0.245 mole, 6 percent excess) of bromine in 200 ml. of carbon tetrachloride at room temperature. The mixture was refluxed for eighteen hours to eliminate hydrogen bromide. After stripping off the carbon tetrachloride more hydrogen bromide was evolved during the distillation of the mixture. The resultant oil was then refluxed with 14 g. (0.25 mole) of potassium hydroxide dissolved in 100 ml. of absolute alcohol. After refluxing for one hour, water was added and two layers separated. The water layer was extracted with ether and the organic layers combined and dried with anhydrous sodium sulfate. The ether was removed on a steam-bath and the remaining oil fractionated through a 6-in. column packed with glass helices. The middle fraction was collected, b.p. 149-155° (1-1.3 mm.), to yield a total of 49 g. (0.167 mole, 72 percent) of colorless liquid. On standing at room temperature white crystals formed. These were removed and the filtrate allowed to remain one week in the refrigerator. The crystalline product was recrystallized

from ethanol, m.p. 88-89° (lit. [10] 88-89°), and has the cis configuration as assigned by Bergmann [15].

The remaining filtrate was then redistilled and a slightly yellow oil collected, b.p. 155-157° (1-1.3 mm). Infrared spectra indicated this product had not more than 30 percent of cis-II as an impurity (Table 1). This was made on the basis of the absorption at 723 $cm.^{-1}$ where the cis isomer has a strong absorption. Attempts to crystallize the oil from pentane both before and after passage through an alumina column proved fruitless (lit. [15] m.p. 43-44°).

Analysis: Calculated for $C_{14}H_{10}BrCl$: C,57.27; H, 3.43.

Found: C, 57.45; H, 3.29

Diphenylacetylene

Diphenylacetylene was prepared according to the method described in Organic Syntheses [16].

1-p-Methoxyphenyl-2-phenylacetylene

This compound was obtained impure using a modification of the method of Orekhoff and Tiffeneau [17].

To an ether solution of benzyl magnesium chloride, prepared from 22.4 g. (0.18 mole) of benzyl chloride and 3.4 g. (0.14 mole) of magnesium, 14 g. (0.10 mole) of p-methoxybenzaldehyde was added over thirty minutes. The solution was refluxed for one hour, cooled, and hydrolyzed with 40 ml. of saturated ammonium chloride solution. The ether and water layers were separated, the water layer extracted with ether and the organic layers combined. The ether was allowed to evaporate and the residual oil was then dehydrated with 50 ml. of

TABLE 1

DATA FOR THE CALCULATION OF cis-1-p-CHLOROPHENYL-1-PHENYL-2-BROMOETHYLENE IN trans-1-p-CHLOROPHENYL-1-PHENYL-2-BROMOETHYLENE

Concentration of cis-II in moles/liter	Optical Density (723 $cm.^{-1}$)	Cell Width (mm)	Extinction Coefficient
1.14×10^{-1}	0.236	0.518	39.8
9.00×10^{-2}	0.214	0.518	45.9
7.89×10^{-2}	0.207	0.518	50.5
1.85×10^{-1}[a]	0.120	0.518	

[a] impure trans-II isomer.

Extinction Coefficient = $E_{Avg.} = 44.1 \pm 2.0$ liters/mole-cm.

Maximum Amount of cis-II in trans-II = 0.120/(42.1)(0.0518) = 0.0551 moles/liter.

Maximum Percent of cis-II in trans-II = (0.0551/0.185)(100) = 29.8 percent.

30 percent sulfuric acid. After refluxing for fifteen hours the mixture was poured into ice water and pale yellow crystals separated. These were recrystalized from ethanol, m.p. 125-130° (lit. [17] 137-138°). This product was assumed to be 1-p-methoxyphenyl-2-phenylethylene.

Six grams (0.028 mole) of this product was brominated with 4.5 g. (0.028 mole) of bromine in 100 ml. of chloroform for forty-five minutes at room temperature. After the addition was completed the chloroform was removed on a steam-bath and a red solid resulted. A total of 7 g. (0.19 mole, 67.7 percent) of 1-p-methoxyphenyl-2-phenyl-1, 2 dibromoethane was obtained, m.p. 170-175° (lit. [17] 175-176°).

In order to effect the elimination of two moles of hydrogen bromide from this compound a variety of bases were used. Two and one-half grams (6.7 mmoles) of the dibromo compound was refluxed for five hours with 1.85 g. (13.4 mmoles) of potassium carbonate in 75 ml. of water. The reaction mixture was then cooled and a reddish-yellow oil separated. The oil was dissolved in ether. After drying with anhydrous sodium sulfate the ether was removed and ethanol added to crystallize the oil. A small amount of yellow-red solid separated, m.p. $\rangle$ 180° (lit. [17] 89-90°).

Potassium hydroxide in absolute ethanol, sodium hydroxide melt, and potassium hydroxide melt were tried to obtain the 89-90° product. In all cases a reddish colored oil was recovered. Adding ethanol resulted in two solids, a yellow solid soluble in hot ethanol

and a red solid insoluble in hot ethanol. The yellow solid had a melting range from 60 to 100°, with most of the solid melting about 60°. The infrared spectrum of this compound was identical to the spectrum of the product (m.p. 57-58°) obtained from the reaction of trans-1-p-methoxyphenyl-1-phenyl-2-bromoethylene (trans-I) with potassium-t-butoxide (described later) except for the absorptions at 965, 895, and 859 cm^{-1}. Absorptions 965 and 859 cm^{-1} correspond to two peaks observed in the infrared spectrum of 1-p-methoxyphenyl-2-phenylethylene. Vapor-phase chromatography, using a Perkin-Elmer Model 154B, showed two peaks for the yellow solid. These peaks had the identical retention times as the peak observed from the product of the potassium-t-butoxide with trans-I reaction and the peak of 1-p-methoxyphenyl-2-phenyethylene. Analysis of the product obtained from the potassium-t-butoxide reaction agreed with the formula of 1-p-methoxyphenyl-2-phenylacetylene. From this it is concluded that the yellow solid is mainly a mixture of 1-p-methoxyphenyl-2-phenylacetylene and 1-p-methoxyphenyl-1-phenylethylene. Attempts to separate these components were unsuccessful.

The red solid melted above 180°. No further identification was attempted.

meso- and dl-Stilbene Dibromide

These compounds were prepared from trans-and cis-stilbene and pyridinium bromide perbromide as described by Fieser [18].

cis-Monobromostilbene

Three and six-tenths grams (0.105 mole) of meso-stilbene dibromide was added to 0.59 g. (0.0105 mole) of potassium hydroxide dissolved in 10 ml. of absolute ethanol. After refluxing for one hour the mixture was cooled, excess water added, and then extracted with two 25 ml. portions of ether. The ether solution was dried over anhydrous sodium sulfate and evaporated under dry nitrogen. A red oil resulted which solidified at 16° (lit. [19] 19°) in an ice-bath.

trans-Monobromostilbene

Eight-tenths of a gram (2.3 moles) of dl-stilbene dibromide was added to 0.13 g. (2.3 mmoles) of potassium hydroxide in 5 ml. of absolute ethanol. The reaction was treated in the same way as in the preparation of cis-monobromostilbene. A light yellow oil was recovered and solidified by dissolving in ethanol and cooling in a dry ice-acetone bath. White crystals, m.p. 29-30° (lit. [19] 32°), were obtained.

t-Butyl Alcohol

t-Butyl alcohol was purified by refluxing with a small amount of sodium for one hour and then distilling through a 3-ft. column packed with stainless steel sponge. The fraction, with a boiling range of 82-82.5°, was collected for use.

Potassium-t-butoxide in t-Butyl Alcohol

Potassium metal, cut under white mineral oil and dipped once in dry pentane, was added to t-butyl alcohol and allowed to dissolve

under dry nitrogen. Concentrations of the solutions were measured by titrating aliquots added to water against standard hydrochloric acid solution using phenolphthalein as the indicator.

Reaction of 1,1-Diphenyl-2-bromoethylene (III) with Potassium-t-butoxide (I)

One gram (3.9 mmoles) of 1,1-diphenyl-2-bromoethylene (III) was dissolved in 50 ml. of dry t-butyl alcohol and 240 mg. (6.1 mmoles) of potassium was added. The reaction was refluxed for seventy-two hours and then quenched by adding nitric acid until the mixture was neutral. Water was added until an oil separated. The oil was dissolved in ethanol to yield 440 mg. (2.5 mmoles, 64 percent) of diphenylacetylene, m.p. 57-58° (lit. [16] 60-61°). An authentic sample of diphenylacetylene mixed with this compound gave no depression in melting point. The infrared spectra of both samples were identical.

Reaction of 1,1-Diphenyl-2-bromoethylene (III) with Potassium-t-butoxide (II)

This reaction was carried out in exactly the same manner as reaction I except that the reaction time was twenty-four hours. Approximately 650 mg. of oil were recovered. Vapor-phase chromatography using a 6-ft. Tide column at a temperature of 190° and a pressure of 10 lbs./sq.in. showed two peaks, retention times 2.7 and 4.7 minutes. Under identical conditions a mixture of III and diphenylacetylene also exhibited two peaks, retention times 2.7 and 4.8 minutes. Prepared trans-monobromostilbene indicated one peak with a retention

time of 7.9 minutes. Cis-monobromostilbene also showed one peak with a retention time of 3.8 minutes. A mixture of cis-monobromostilbene and III gave only one broad peak. A broad peak was also observed with the reaction mixture and the cis-isomer at approximately the same retention time. Attempts to resolve these broad peaks were unsuccessful. The infrared spectrum of the reaction mixture was identical to an infrared obtained from a mixture of III and diphenylacetylene. Cis-monobromostilbene had several peaks (2900, 1360, 1190, 1095, 890, and 792 $cm.^{-1}$) which did not appear in the infrared spectrum of the reaction mixture.

Reaction of 1-p-Methoxyphenyl-1-phenyl-2-bromoethylene (I) and Potassium-t-butoxide

One gram (3.5 mmoles) of trans-I was dissolved in 25 ml. of a 0.40 M (10 mmoles) solution of potassium-t-butoxide in t-butyl alcohol. The reaction mixture was refluxed for six days. After neutralizing with hydrochloric acid and extracting with ether, 500 mg. (2.4 mmoles, 69 percent) of yellow-white crystals (m.p. 53-58°) resulted on evaporation of the ether extract. These were recrystalized from ethanol to give a white crystalline product, m.p. 57-58° (lit. [17] 89-90°). Similar results were obtained with the cis-I isomer.

Analysis: Calculated for $C_{15}H_{12}O$: C, 86.54; H, 5.75

Found: C, 86.56; H, 5.82.

Reaction of 1-*p*-Chlorophenyl-1-phenyl-2-bromoethylene (II) with Potassium-*t*-butoxide

Fifty-four hundredths of a gram (1.84 mmoles) of *cis*-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene (*cis*-II) was refluxed for sixty-nine hours with a large excess of potassium-*t*-butoxide in 20 ml. of *t*-butyl alcohol. Following this, water was added to the reaction mixture until it became cloudy. After placing the mixture in a refrigerator for two days, 240 mg. (1.1 mmoles, 61.5 percent) of 1-*p*-chlorophenyl-2-phenylacetylene was recovered. Recrystallization from ethanol gave a pure product, m.p. 81-83° (lit. 10 82-83°), as evidenced by one peak recorded by vapor-phase chromatography.

Reaction of 1-*p*-Methoxyphenyl-1-phenyl-2-bromoethylene (I) with Sodium Ethoxide

Two hundred and thirty milligrams (0.79 mmole) of *trans*-I was refluxed for forth-eight hours with 100 mg. (4.35 mmoles) of sodium in 15 ml. of absolute ethanol. Water was added to quench the reaction and crystals separated which were identical with the starting material as evidenced by the melting point, 79-81°, and a mixed melting point. *Cis*-I gave similar results.

Reaction of *trans*-1-*p*-Methoxyphenyl-1-phenyl-2-bromoethylene (*trans*-I) with Potassium-*t*-amylate

Two hundred milligrams (0.69 mmole) of *trans*-I was treated with 150 mg. (3.94 mmoles) of potassium in 20 ml. of *t*-amyl alcohol for sixty-one hours at reflux temperature. Water was added to the reaction

mixture and white crystals separated, m.p. 45-90°. These were not characterized further.

Reaction of trans-1-p-Methoxyphenyl-1-phenyl-2-bromoethylene (trans-I) with Potassium-t-butoxide in Diglyme

Five hundred milligrams (1.73 mmoles) of trans-I was treated with 300 mg. (2.68 mmoles) of potassium-t-butoxide in diglyme solvent for ninety-six hours at reflux temperature. The addition of water resulted in an oil which was separated from the other liquid and dissolved in ethanol. White crystals separated, m.p. 45-90°, and were not characterized further.

Reaction of trans-1-p-Methoxyphenyl-1-phenyl-2-bromoethylene (trans-I) with Potassium Amide in Liquid Ammonia

One and one-tenth grams (3.8 mmoles) of trans-I was dissvoled in 40 ml. of dry ether and added dropwise to 1.0 g. (18.2 mmoles) of potassium amide in 150 ml. of liquid ammonia. After the addition, the solution was allowed to evaporate overnight. Water and ether were added to the residue and a reddish-white solid was obtained from the ether layer. Recrystallization from ethanol yielded a white solid, m.p. 48-50°. The infrared spectrum showed the presence of $-C\equiv C-$ at 2225 $cm.^{-1}$. Vapor-phase chromatography showed one peak at the same retention time as an authentic sample of 1-p-methoxyphenyl-2-phenylacetylene run under identical conditions.

Reaction of cis-1-p-Methoxyphenyl-1-phenyl-2-bromoethylene with Phenyl-lithium in Ether

Two hundred milligrams (0.69 mole) of cis-I was treated with 10 ml. of 0.23 M (2.3 mmoles) of phenyl-lithium in dry ether for two hours at reflux temperature. After the removal of ether, water and hydrochloric acid were added to the residual oil. Yellow-white crystals separated, m.p. 50°. Vapor-phase chromatography indicated this was starting material.

Attempted Rearrangement of trans-1-p-Methoxyphenyl-1-phenyl-2-bromoethylene (trans-I) to cis-1-p-Methoxyphenyl-1-phenyl-2-bromoethylene with Ultraviolet Light

Three hundred milligrams (1.04 mmoles) of trans-I was dissolved in 20 ml. of ethanol and placed under an ultraviolet lamp for eight hours. Water was added and yellow-white crystals separated, m.p. 76-78°. The crystals were redissolved in ethanol and placed under the lamp for an additional fifteen hours. The solution was treated as before. A solid, m.p. 75-78°, and oil were recovered. Some impure crystals were obtained from the oil, m.p. 70-80°. To the mother liquor, after the separation of solid and oil, ether was added, separated from the water layer, dried with anhydrous sodium sulfate and evaporated almost to dryness. Ethanol was added and some crystals were recovered, m.p. 79-81°.

B. Spectra

1. Ultraviolet Absorption Spectra

Ultraviolet absorption spectra were employed to determine the concentrations of starting materials and products used in the kinetic measurements. Ninety-five percent ethanol was used as our solvent. A scan of the spectra from 340 mμ to 220 mμ by the use of the Beckman DK-2 Spectrophotometer indicated the maximum absorptions for our materials. The extinction coefficients for each of the maxima needed for our concentration calculations were determined utilizing the Beckman Model DU. Table 2 summarizes the maxima observed for each of our compounds used in kinetic measurements. In cases where there are several maxima the largest two are given.

Data for the calculation of the extinction coefficients of tolans formed from the reactions as well as some of the starting materials are summarized in Tables 3, 4, 5, 6, and 7.

2. Visible Absorption Spectra

It was desirable to follow the formation of bromide ion in the kinetic measurements. Since the concentration of starting material was approximately 10^{-3} M an accurate method of determining bromide ion was desirable. Accordingly, the method used by Goldman and Byles was tried [20]. The principle of the method was the oxidation of bromide ion with chloramine T reagent and the bromination of phenol red in a buffer solution. A color comparison of brominated compound versus distilled water was made with a Beckman DU Spectrophotometer at 590 mμ. The brominated compound should appear reddish to

TABLE 2

ABSORPTION MAXIMA OF COMPOUNDS USED IN KINETIC MEASUREMENTS

Compounds	Maxima (mμ)	
1-*p*-methoxyphenyl-2-phenylacetylene	306	287
cis-1-*p*-methoxyphenyl-1-phenyl-2-bromoethylene	268	248
trans-1-*p*-methoxyphenyl-1-phenyl-2-bromoethylene	269	254
1-*p*-chlorophenyl-2-phenylacetylene	302	284
cis-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene	259	235
trans-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene	not determined due to impurities	
diphenylacetylene	296.5	279
1,1-diphenyl-2-bromoethylene	259	

TABLE 3

EXTINCTION COEFFICIENT DETERMINATION FOR
1-p-METHOXYPHENYL-2-PHENYLACETYLENE

Concentration in moles/liter x 10^5	Optical Density (306 mμ)	Extinction Coefficient x 10^{-4}
1.73	0.351	2.02
3.46	0.698	2.02
4.34	0.865	1.98
1.00	0.206	2.06
0.10	0.021	2.01
2.00	0.404	2.02

$E = \text{Extinction coefficient}_{Avg.} = 2.02 \pm 0.007 \times 10^4$ (306 mμ)

TABLE 4

EXTINCTION COEFFICIENT DETERMINATION FOR
trans-1-p-METHOXYPHENYL-1-PHENYL-2-BROMOETHYLENE

Concentration in moles/liter x 10^4	Optical Density (306 mμ)	Extinction Coefficient x 10^{-3}
0.701	0.136	1.93
2.61	0.521	1.99
1.31	0.263	2.02
2.09	0.409	1.96

$\text{Extinction Coefficient}_{Avg.} = 1.98 \pm 0.015 \times 10^3$ (306 mμ)

TABLE 5

EXTINCTION COEFFICIENT DETERMINATION FOR
cis-1-p-METHOXYPHENYL-1-PHENYL-2-BROMOETHYLENE

Concentration in moles/liter x 10^4	Optical Density (306 mμ)	Extinction Coefficient x 10^{-3}
1.22	0.139	1.14
2.44	0.267	1.09
3.63	0.422	1.16
2.61	0.296	1.14
1.31	0.154	1.16

$E = \text{Extinction Coefficient}_{Avg.} = 1.14 \pm 0.01 \times 10^3$ (306 mμ)

TABLE 6

EXTINCTION COEFFICIENT DETERMINATION FOR
1-p-CHLOROPHENYL-2-PHENYLACETYLENE

Concentration in moles/liter x 10^5	Optical Density (302 mμ)	Extinction Coefficient x 10^{-4}
0.764	0.190	2.48
1.53	0.409	2.68
0.580	0.153	2.64
0.725	0.182	2.52

$E = \text{Extinction Coefficient}_{Avg.} = 2.58 \pm 0.03 \times 10^4$ (302 mμ)

TABLE 7

EXTINCTION COEFFICIENT DETERMINATION
FOR DIPHENYLACETYLENE

Concentration in moles/liter x 10^5	Optical Density (296.5 mμ)	Extinction Coefficient x 10^{-4}
1.74	0.421	2.42
3.47	0.870	2.51
2.61	0.650	2.50
1.84	0.459	2.49

$E = \text{Extinction Coefficient}_{\text{Avg.}} = 2.48 \pm 0.015 \times 10^4$ (296.5 mμ)

violet, depending upon its concentration. By constructing a calibration curve of bromide ion concentration from 0.1 to 1.0 mg./l. versus optical density at 590 mμ a sharp differentiation within ± 1 percent can be made between varying quantities of bromide.

C. Kinetic Methods

1. Ultraviolet Absorption Method

Essentially the kinetic method described by Pritchard and Bothner-By [9] was used. The reactions of 1,1-diaryl-2-bromoethylenes with potassium-t-butoxide in t-butyl alcohol were carried out as follows.

Standard base was prepared as previously described. Glassware used was washed twice with acetone, once with tap water, then with distilled water, and then dried in an oven at 135°.

Weighed amounts of 1,1-diaryl-2-bromoethylenes were accurately diluted to a standard volume with t-butyl alcohol. Twenty-five milliliter samples were added to a 50 ml. volumetric flask and standard base was added until the total volume was 50 ml. The contents of the flask were thoroughly mixed and added to a 50 ml. buret. Five milliliter samples were then added to 10 ml. ampoules, previously flushed with dry nitrogen, using a needle on the tip of the buret in order to obtain a fine stream of liquid. The ampoules were capped with medicine dropper tops, after flushing again with dry nitrogen, and placed in an ice-bath. The tubes were then sealed, preheated in a water bath for 20 seconds at ca. 95° and immediately transferred to a constant temperature mineral oil bath, which was maintained at a temperature

of $95^{\circ} \pm 0.02^{\circ}$. The purpose of preheating the frozen tubes was to eliminate the large drop in temperature in the mineral oil bath which would result from adding the tubes directly. Zero time was taken when the tubes were placed in the bath. Ampoules were withdrawn at intervals and quenched by placing in an ice-bath. While frozen the tubes were opened and distilled water added to convert any potassium-t-butoxide remaining to potassium hydroxide. The tubes were then allowed to warm to room temperature and the solution transferred to a volumetric flask. The tubes were rinsed once with ethanol and once with distilled water. After accurately diluting with ethanol to a standard volume at room temperature the ultraviolet spectra were run versus ethanol as a blank.

Optical densities were measured at wave lengths corresponding to maxima of tolans. These were selected because starting olefins either absorbed very little or did not absorb at all at these wave lengths.

Concentrations were calculated from Beer's Law, assuming the formation of product is equal to the disappearance of starting material. The general equation $A = abc$, was used, where

A = absorbance or optical density of the solution,

a = molar extinction coefficient of the solute,

b = thickness of the cell containing the solution, and

c = concentration of the solution in moles/liter.

For the reactions of trans- and cis-1-p-methoxyphenyl-1-phenyl-2-bromoethylene (I), which absorbed slightly at the maximum of

1-p-methoxyphenyl-2-phenylacetylene, the following modified equation was used:

$$A_{Total} = a_T bc_T + a_{EH} bc_{EH},$$

where Total refers to 1-p-methoxyphenyl-2-phenylacetylene (tolan) and cis- or trans-I. T represents p-methoxytolan and EH refers to cis- or trans-I.

Knowing the concentration of starting material the relation $c_T + c_{EH}$ = constant was used to substitute in the equation and determine the concentration of product or starting material during the reaction.

A plot of -log c_{EH} versus time gave a straight line, indicative of a first-order reaction. Values of k were calculated by the method of least squares [21].

2. Vapor-phase Chromatography

Quantitative analyses of mixtures of 1,1-diphenyl-2-bromoethylene and diphenylacetylene were made in the anticipation of following the rate of the reactions by the use of vapor-phase chromatography. Samples were accurately weighed, dissolved in chloroform and injected into a vapor-phase fractometer, Perkin-Elmer Model 154. A 6-ft. Tide column at temperature ca. 180° and a pressure of 25 lbs./sq.in. (helium) was used to separate the mixtures. The areas under the curves for each component were measured by constructing triangles over the curves and calculating the areas of the triangles. Table 8 summarizes the results obtained. This method of analyses was not used in the kinetic measurements.

TABLE 8

QUANTITATIVE ANALYSIS OF 1,1-DIPHENYL-2-BROMOETHYLENE AND DIPHENYLACETYLENE MIXTURES BY VAPOR-PHASE CHROMATOGRAPHY

	Mole percent of 1,1-Diphenyl-2-bromoethylene			Mole percent of Diphenylacetylene		
Calculated	77.4	60.6	41.9	22.6	39.4	58.1
Measured	78.5	59.2	44.1	21.5	40.8	55.9

D. Dipole Moments

1. Apparatus

Dipole moments were obtained by measuring the dielectric constant of dilute solutions in benzene, a nonpolar solvent. The dielectric constant D was determined by measuring the ratio of the capacity of a condenser with the substance between the plates of a cell compared to the capacity of the condenser with a vacuum between the plates of a cell.

Capacities of the cell were measured by balancing a General Radio Company type 716-C capacitance bridge containing the measuring cell (unknown capacitor) and a precision capacitor (balancing capacitor). These measurements were made at frequencies of 90 and 70 kilocycles obtained by a General Radio Company oscillator type 1302-A. Null or balance points were found by observing the smallest sine wave on a Tektronix type 541-A oscilloscope. A J.C. Balsbaugh 2TN50 cell was used for measurements. The volume of liquid used in this cell was ca.15 ml. The cell was immersed in a water bath held at 25° ± 0.02°. Since the temperature of the room was ca. 24° little heating was necessary to maintain the temperature. It was found that shielding the thermoregulator, stirring motor and heater from the cell with a 10" x 10" x 1/8" piece of copper metal removed any interference observed on the oscilliscope.

Readings of capacitance were made after the solutions had 10 minutes to reach equilibrium. Five readings were taken at each point.

Refractive indices of the solutions were measured with an Abbe refractometer held at 25° ± 0.02°.

Densities of the solutions were determined with a 5 ml. pycnometer calibrated with distilled water. The pycnometer was filled at ca. 20° and immersed in a constant temperature bath, 25° ± 0.02°, for ten minutes. After removing, it was carefully dried and weighed. Densities were not corrected for the buoyancy of air.

Solutions were made up by weighing both solute and benzene for the first sample and then accurately diluting this sample with volumetric pipets in a room at ca. 20° to obtain the other solutions. Five solutions were prepared for each compound. These ranged from 0.015 to 0.002 mole fraction of solute (x_2).

2. Materials

Pure benzene previously prepared for dielectric studies was used, $n_D^{25°} = 1.4982$, $d^{25°} = 0.8736$.

Spectral grade carbon tetrachloride was used.

The purest available samples of cis- and trans-1-p-methoxyphenyl-1-phenyl-2-bromoethylene were used.

3. Calculations

a. Molar Refraction

Molar refractions of the solutions were calculated according to the equation

$$R_{12} = \frac{n^2 - 1}{n^2 + 2} \frac{x_1M_1 + x_2M_2}{d_{12}},$$

where R_{12} is the molar refraction of the mixture, n is the refractive index, x_1 and x_2 are the mole fractions of solvent and solute respectively, and M_1 and M_2 are the molecular weights of solvent and solute. d_{12} is the density of the solution.

The values of R_{12} were determined from the equation

$$R_{12} = x_1R_1 + x_2R_2,$$

where R_1 and R_2 are the molar refractions of solvent and solute, respectively.

b. Dielectric Constant

The total capacitance of a cell is made up of the capacitance of the cell leads C_L and the capacitance of the cell when filled sith a substance DCo. When the capacitance of the cell is measured with air (D = 1.000), and with benzene of a known dielectric constant (D = 2.273 at 25°) [22] the cell constants may be determined and used in the measurement of the dielectric constant of an unknown material. The following standardization was made:

Capacity with air in cell = 143.35 mmf. = $C_o + C_L$

Capacity with benzene in cell = 177.6 mmf. = $2.273C_o + C_L$

(mmf. = micromicrofarads).

From these two equations,

$1.273C_o = 34.25$

$C_o = 26.90$ mmf.

$C_L = 116.45$ mmf.

To check the standardization pure carbon tetrachloride was placed in the cell and its dielectric constant calculated.

Capacity with CCl_4 in cell = 176.4 mmf.

$176.4 = \left[(D)(26.90)\right] + 116.45$

$D_{CCl_4} = 2.228$ (lit. [22] = 2.227)

c. Dipole Moment

The dipole moment μ was calculated using the equation

$$\mu = 0.01281 \times 10^{-18} \quad (P_{2\infty} - R_2)T^{1/2}$$

where R_2 is the molar refraction of the solute, T is the absolute temperature and $P_{2\infty}$ is the polarization of the solute at infinite dilution. $P_{2\infty}$ was determined by the method of Hendestrand [23] using the equation

$$P_{2\infty} = \frac{(D_1 - 1)(M_2 - M_1\beta)}{(D_1 + 2)d_1} + \frac{3M_1D_1\alpha}{d_1(D_1 + 2)^2}$$

where the symbols have the usual significance. β and α are the slopes of the lines obtained from the following equations:

$$D_{12} = D_1(1 - \alpha x_2)$$

$$d_{12} = d_1(1 + \beta x_2)$$

D_{12} and d_{12} are the dielectric constants and densities of the solutions. These slopes were calculated by the method of least squares.

CHAPTER III

RESULTS

Dipole Moments

The dipole moments of the cis and trans isomers of 1-p-methoxyphenyl-1-phenyl-2-bromoethylene were measured. The trans configuration was assigned to the higher melting isomer and the cis configuration to the lower melting isomer on the basis of the observed moments as compared to the calculated moments. These results are summarized in Table 9. Figures 1 and 2 were used to determine α and β used in the calculation of the dipole moments. α and β are the slopes of the lines in Figures 1 and 2, as determined by the method of least squares [21].

Syntheses

Five compounds were prepared for kinetic measurements. These were the cis and trans isomers of 1-p-methoxyphenyl-1-phenyl-2-bromoethylene (cis- and trans-I), the cis and trans isomers of 1-p-chlorophenyl-1-phenyl-2-bromoethylene (cis- and trans-II) and 1,1-diphenyl-2-bromoethylene (III). All were obtained pure, except trans-II which was contaminated with a maximum of 30 percent of cis-II as calculated quantitatively by infrared spectra.

Cis- and trans-monobromostilbene, products of possible intermediates in the reaction of 1,1-diphenyl-2-bromoethylene, were also prepared.

TABLE 9

DATA FOR THE DETERMINATION OF DIPOLE MOMENTS OF cis- AND trans-1-p-METHOXYPHENYL-1-PHENYL-2-BROMOETHYLENE (I)

trans-1-p-Methoxyphenyl-1-phenyl-2-bromoethylene

Solution No.	Moles of Solute x 10^3	Moles Solvent	Mole Fraction of Solute x 10^2	Mole Fraction of Solvent	Dielectric Constant (D)	Density	Index of Refraction
Benzene	---	---	---	----	2.2730	0.8736	1.4982
1	3.382	0.2234	1.4910	0.98509	2.3994	0.8893	1.5031
2	1.691	0.2234	0.7513	0.00249	2.3343	0.8804	1.5004
3	0.846	0.2234	0.3770	0.99623	2.3156	0.8759	1.4990
4	0.423	0.2234	0.1885	0.99811	2.2953	0.8750	1.4984

R_2 = 79.76 α = 8.423 β = 1.213 $P_{2\infty}$ = 223.5 μ = 2.65 debye units

cis-1-p-Methoxyphenyl-1-phenyl-2-bromoethylene

Solution No.	Moles of Solute x 10^3	Moles Solvent	Mole Fraction of Solute x 10^2	Mole Fraction of Solvent	Dielectric Constant (D)	Density	Index of Refraction
1	3.8292	0.2234	1.685	0.98314	2.3808	0.8925	1.5041
2	1.9146	0.2234	0.8498	0.99151	2.3325	0.8829	1.5010
3	0.9573	0.2234	0.4267	0.99572	2.3102	0.8781	1.4995
4	0.4786	0.2234	0.2138	0.99786	2.2953	0.8755	1.4984

R_2 = 79.0 α = 5.882 β = 1.224 $P_{2\infty}$ = 176.0 μ = 2.18 debye units

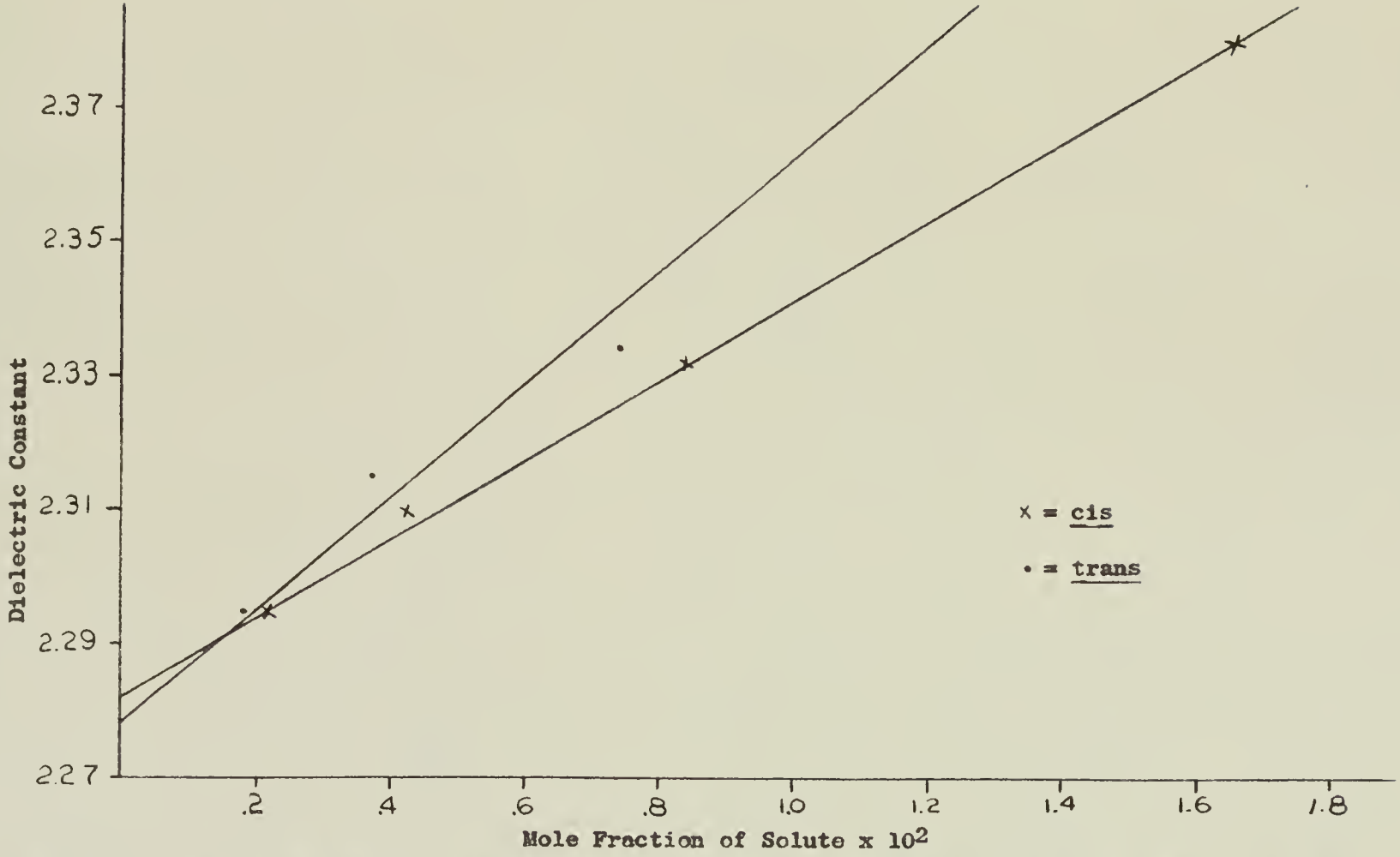


Figure 1. Determination of α for cis- and trans-1-p-methoxyphenyl-1-phenyl-2-bromoethylene.

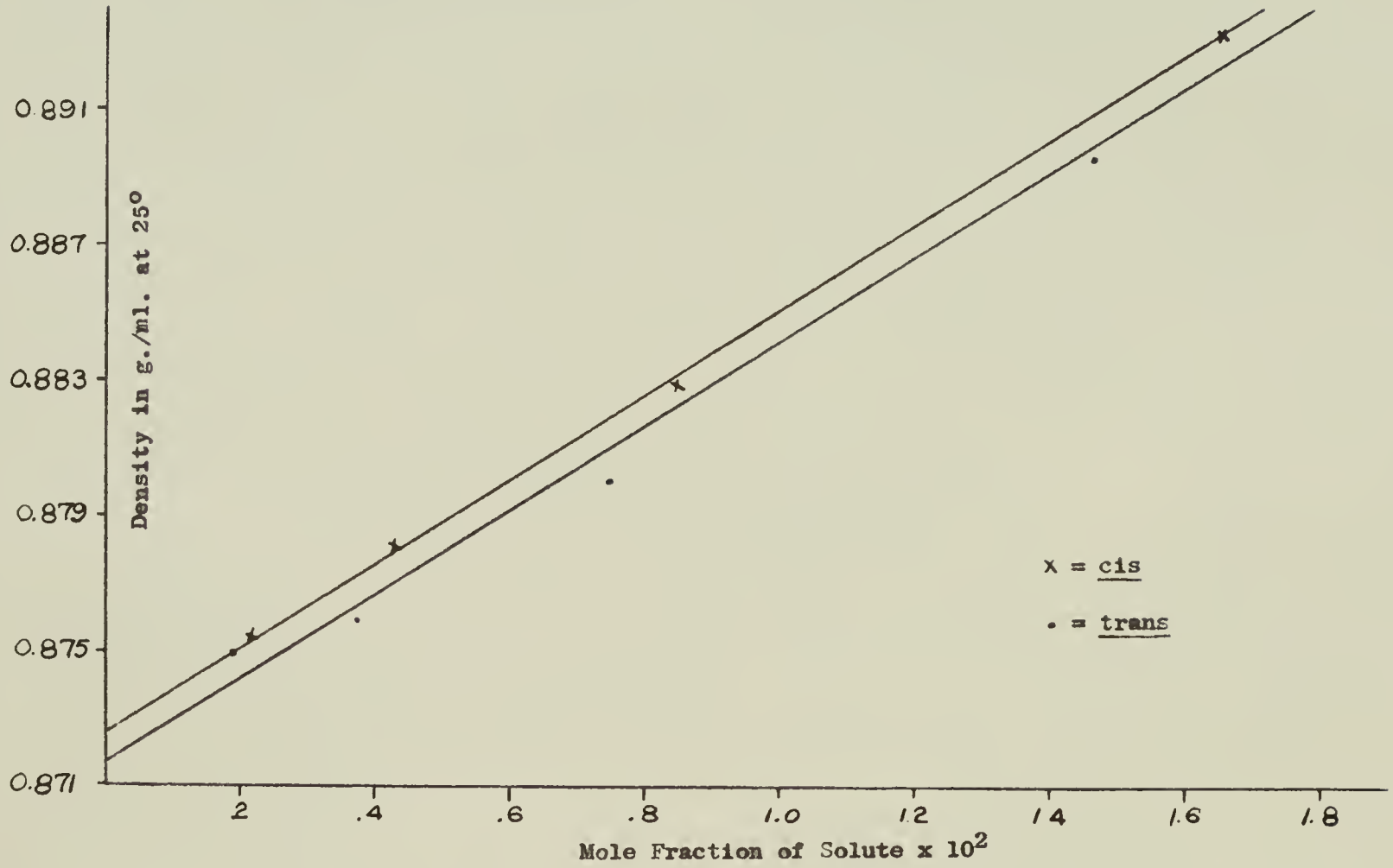


Figure 2. Determination of β for cis- and trans-1-p-methoxyphenyl-1-phenyl-2-bromoethylene.

Products from the reactions of 1,1-diphenyl olefin (III) and cis and trans-p-methoxy compounds (I) with potassium-t-butoxide were synthesized by an alternate route. They were diphenylacetylene and 1-p-methoxyphenyl-2-phenylacetylene (obtained impure).

Product Analysis

All results indicate that the reactions of the bromoethylenes with potassium-t-butoxide give mainly diphenyl and substituted diphenylacetylenes (tolans). Thus, spectroscopic analysis indicated at least 85 percent of the reaction yielded tolans for all of the starting bromoethylenes (e.g. see Table 10). Furthermore, the reaction of 1,1-diphenylolefin (III) with excess base gave a 64 percent yield of diphenylacetylene, after recrystallization. Trans- and cis-p-methoxy compounds (I), when reacted with potassium-t-butoxide, yielded 69 and 62 percent respectively, of essentially pure tolans.

A careful analysis of the crude reaction mixture, resulting from the incomplete reaction of 1,1-diphenyl olefin (III) with potassium-t-butoxide, indicated it consisted only of starting material and diphenylacetylene. This mixture was analyzed by:

1. Comparing the vapor-phase chromatograms of the reaction mixture and a mixture of 1,1-diphenyl olefin (III) and diphenylacetylene.

2. Preparing cis- and trans-monobromostilbene, two possible products from intermediates in the reaction of 1,1-diphenyl olefin (III) with base, and comparing their vapor-phase chromatograms and infrared spectra to those of the reaction mixture.

3. Comparing the infrared spectrum of the reaction mixture to the spectra of the starting material and diphenylacetylene.

Kinetics

Since spectroscopic evidence indicates that all of the olefins gave over 85 percent of the tolan, the reaction may reasonably be described by

$$\frac{dC_T}{dt} = \frac{-dC_{EH}}{dt} = k_{obs.}C_{EH},$$

where C_T and C_{EH} are molar concentrations of tolan and bromoethylene derivatives, respectively, and $k_{obs.}$ is the observed rate constant for the reaction. A plot of -log C_{EH} versus t (time) gave a straight line representative of a first-order reaction in all cases. Values of k were calculated from the slope of the lines by the method of least squares [21]. Table 10 indicates the typical data used in the kinetic runs.

The kinetic results of the five compounds studied are summarized in Table 11. The same base concentration (ca. 0.20 M) was used in all cases to eliminate any differences in the rate constants resulting from the base term inherent in these constants and to minimize differences in salt effects between compounds. Three runs were made for each compound except 1,1-diphenyl-2-bromoethylene, whose rate constant was previously reported under very similar conditions [7]. A concentration of ca. 1.0×10^{-3} M of starting material was used. In cases where this varied the pseudo-first-order rate constant remained essentially the same.

TABLE 10

KINETIC DATA FOR THE REACTION OF *trans*-1-*p*-METHOXYPHENYL-1-PHENYL-2-BROMOETHYLENE (*trans*-I) WITH 0.20 M POTASSIUM-*t*-BUTOXIDE AT 95°

Sample No.	Optical Density (306 mu)	Concentration of *trans*-I in moles/liter x 10^3	Time (minutes)
0[a]	0.291	1.462[b]	0
1	0.123	1.280	74
2	0.163	1.172	134
3	0.206	1.059	198
4	0.236	0.975	253
5	0.310	0.855	320
6	0.511	0.220	1162

[a] 1 ml. of sample to 9 ml. of solvent. All others were diluted 1 ml. of sample to 49 ml. of solvent.

[b] Measured initial concentrations were within 5 percent of those calculated by weighing of samples and diluting to standard volume.

TABLE 11

SUMMARY OF KINETIC DATA FOR THE REACTIONS OF 1,1-DIARYL-2-BROMOETHYLENES (EH) WITH POTASSIUM-*t*-BUTOXIDE (KB) AT 95°

Material	Concentration of KB in moles/liter	Concentration of EH in moles/liter x 10^3	k(min.$^{-1}$) x 10^3
trans-1-*p*-methoxyphenyl-1-phenyl-2-bromoethylene	0.197	1.47	1.56
	0.200	1.46	1.62
	0.201	1.47	1.98
cis-1-*p*-methoxyphenyl-1-phenyl-2-bromoethylene	0.197	1.62	0.99
	0.200	1.58	1.06
	0.201	1.61	1.08
trans-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene[a]	0.190	1.39	0.45
	0.202	1.39	0.40
	0.212	1.03	0.50
cis-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene	0.190	0.88	0.93
	0.202	0.88	1.05
	0.206	0.12	1.13
1,1-diphenyl-2-bromo-ethylene[b]	0.206	1.16	0.84
	0.212	1.12	0.85

[a] *trans*-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene was contaminated with a maximum of 30 percent of *cis*-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene.

[b] A $k_{obs.}$ of 0.85 x 10^{-3} (min.$^{-1}$) at 0.212 M KB agrees well with a reported $k_{obs.}$ of 0.73 x 10^{-3} (min.$^{-1}$) at 0.215 M KB [9].

A characteristic plot of -log C_{EH} versus time (minutes) is shown in Figure 3.

It is desirable to compare the rate constants of the bromoethylenes with each other. For that purpose Figure 4 was drawn. Since the rate constants are independent of the concentration of bromoethylenes, the average rate constants of each compound are used to determine the average slopes of the lines in Figure 4. The base concentration of 0.20 M was used. The calculated rate constants of 1.62, 1.06, 0.45, 1.04, 0.82 x 10^{-3} for trans- and cis-p-methoxy compounds (I), trans- and cis-p-chloro compounds (II) and 1,1-diphenyl olefin (III), respectively, were used. A distinct difference of slopes, except between cis-p-methoxy-I and cis-p-chloro-II, can be observed in each case.

Reactions with Other Bases

A few bases, other than potassium-t-butoxide in t-butyl alcohol were tried to effect the rearrangement. Treatment of cis- or trans-1-p-methoxy compounds (I) with sodium ethoxide in ethanol and phenyllithium in ether gave no 4-methoxytolan. Potassium amide, in liquid ammonia, was successful while potassium-t-amylate in t-amyl alcohol and potassium-t-butoxide in diglyme (diethylene glycol dimethyl ether) gave dubious results.

Miscellaneous Experiments

Attempted rearrangement of trans-p-methoxy-I to cis-p-methoxy-I under ultraviolet radiation was unsuccessful.

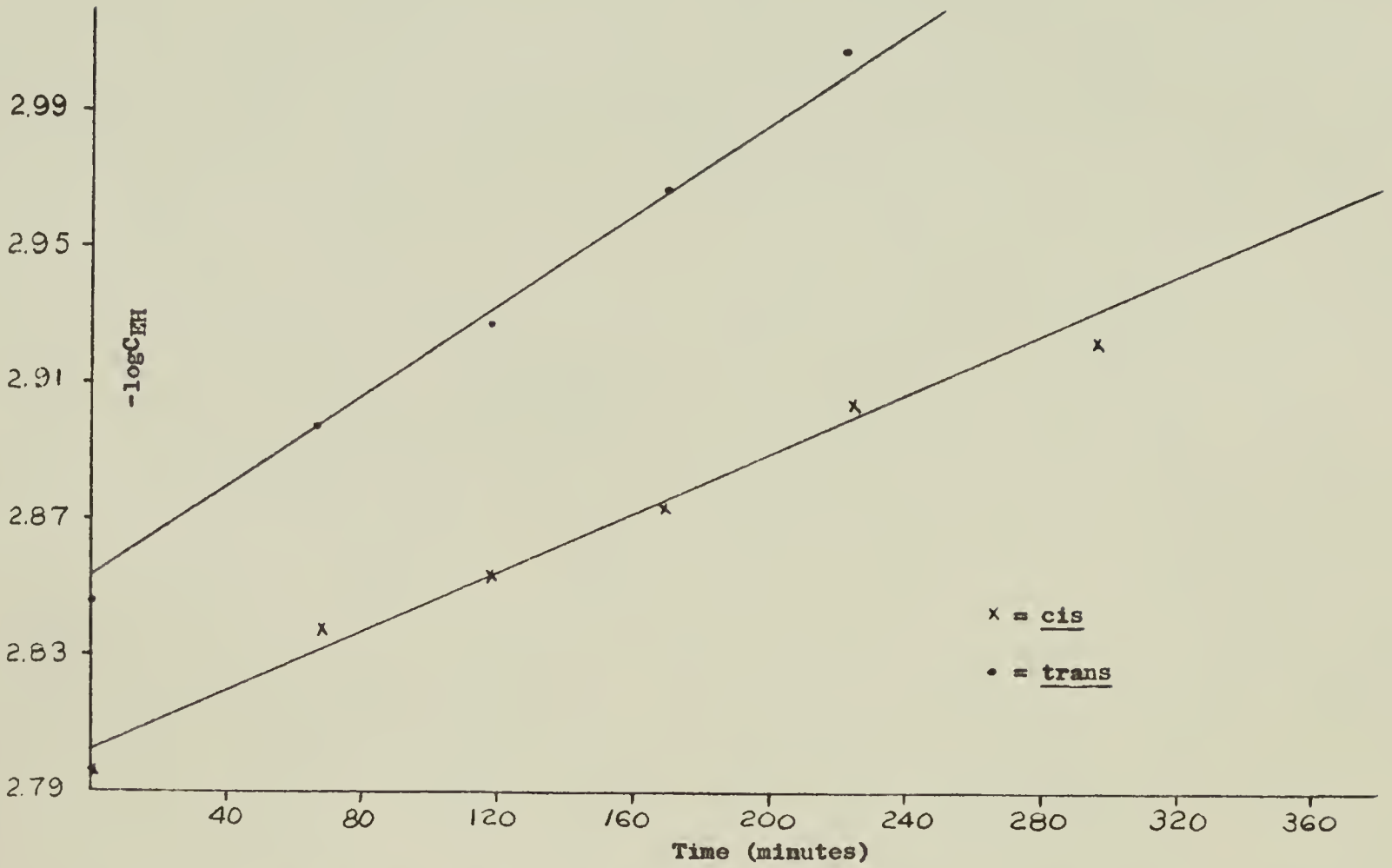


Figure 3. Reaction of trans- and cis-1-p-methoxyphenyl-1-phenyl-2-bromoethylene (I) with 0.197 M Potassium t-butoxide at 95°.

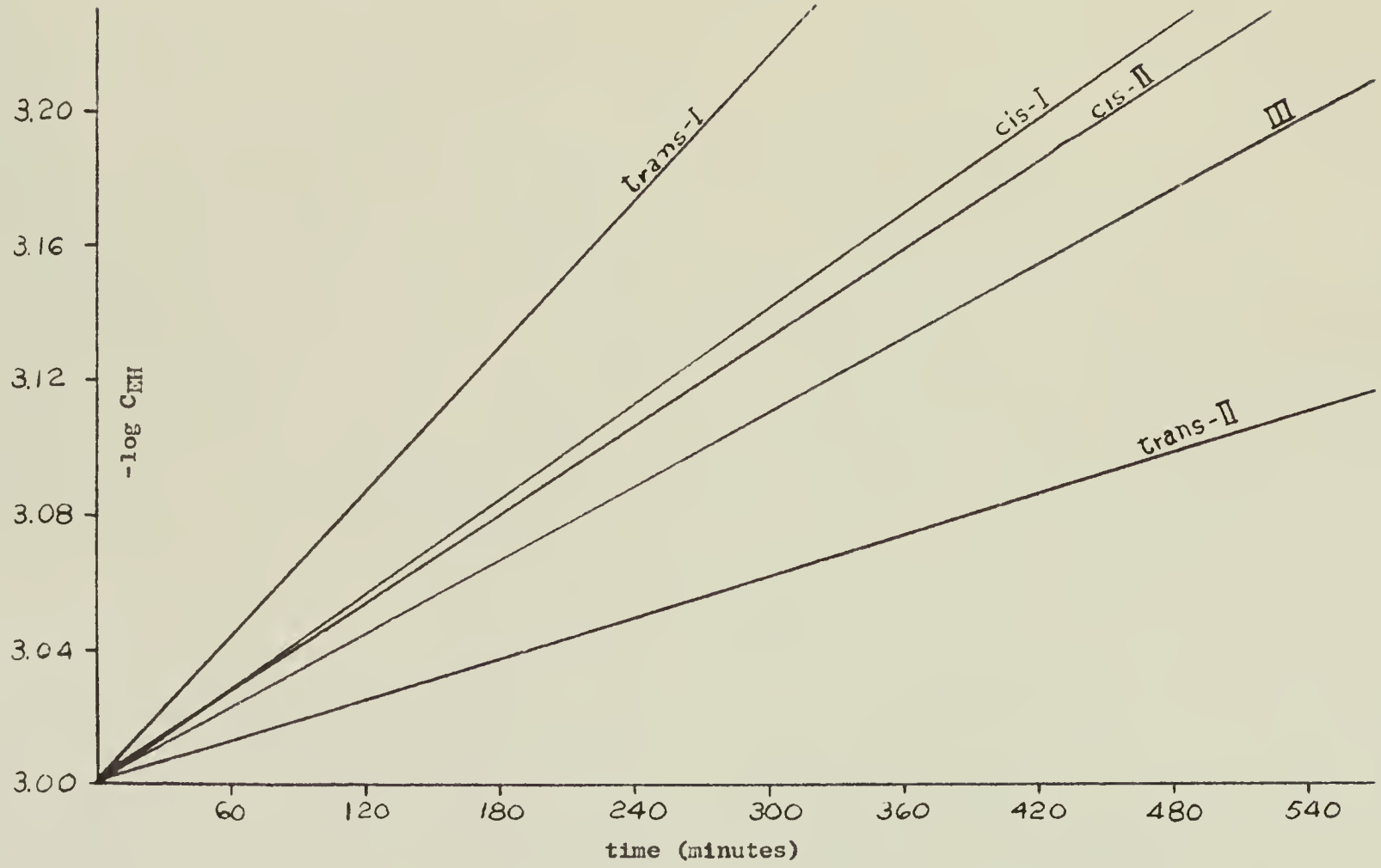


Figure 4. Comparison of rate constants of 1,1-diaryl-2-bromoethylenes at 0.20M potassium-t-butoxide.

A quantitative method of calculating the percent of 1,1-diphenyl-2-bromoethylene and diphenylacetylene by vapor-phase chromatography was developed and found to be accurate within $\pm$ 1 mole percent.

CHAPTER IV

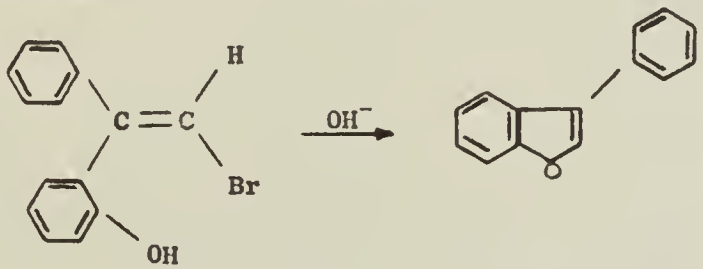
DISCUSSION OF RESULTS

Dipole Moments

In order to interpret the relative reaction rate constants and properly discuss reaction mechanisms the proper geometric configuration of the isomers of 1-p-methoxyphenyl-1-phenyl-2-bromoethylene (cis- and trans-I) and of the isomers of 1-p-chlorophenyl-1-phenyl-2-bromoethylene (cis- and trans-II) must be known. Usually the best way to assign these configurations is by dipole moment measurements. This has been done for cis- and trans-II and the higher melting isomer was found to have the cis configuration (bromine and p-chlorophenyl cis) [15].

Stoermer and Simon [12], who first prepared the cis- and trans-p-methoxy compounds (I), assigned the trans configuration to the higher melting isomer. Their assignment was based on two assumptions:

1. The one isomer of 1-phenyl-1-o-hydroxyphenyl-2-bromoethylene, which reacts with base to yield 2-phenylbenzofuran, necessarily has the cis configuration.



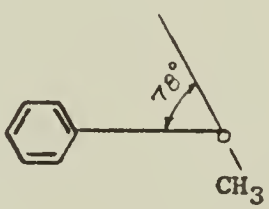
2. Since this isomer was lower melting, the trans configuration could be assigned to all the higher melting isomers of 1,1-diaryl-2-bromoethylenes with a substituent in one of the benzene rings. These assumptions are not valid in all cases, as evidenced by the cis-p-chloro compound (II) being the higher melting isomer of the isomers of cis- and trans-p-chloro compounds. Thus, a determination of the dipole moments of the cis and trans-p-methoxy compounds (I) was undertaken.

Theoretical dipole moments were calculated upon the following assumptions:

1. The carbon-bromine bond moment is 1.38 debye units, the value assigned by Smyth [24].

2. The bond moment of the vinyl hydrogen is taken as zero because Gent [25] has stated the carbon-hydrogen bond moment is ca. zero in ethylene.

3. The moment of the p-methoxyphenyl group is 1.25 debye units, the same as that reported for anisole [26]. The moment angle of the methoxy group is 78° from the line of attachment to the benzene nucleus and at a direction into the benzene ring [27].



A further assumption made here is the free rotation of the methoxymethyl group around the carbon-oxygen bond resulting in the rotation of the methoxy-moment around the line of attachment to the benzene ring.

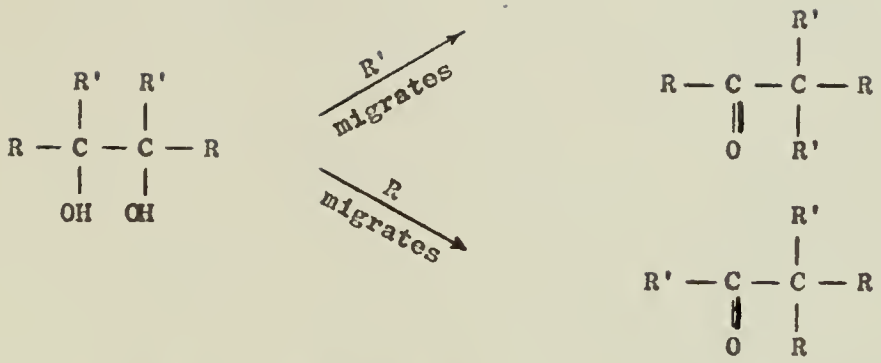
4. All other moments in the molecule are zero.

5. The bond angles are not distorted from their normal values.

Using these assumptions the dipole moments of the cis- and trans-p-methoxy compounds (I) were calculated by the law of cosines. In the case of trans-I the moment of the methoxy group is always 78° from the carbon-bromine moment. In the cis isomer the angle between the methoxy moment and the carbon-bromine moment varies from a minimum of 42° to a maximum of 162° when the methoxy moment rotates. The calculated value of cis-I is taken as the average of the maximum and minimum values. The calculated dipole moment of the trans-p-methoxy compound (I) is 2.05 debye units, while the calculated value of the cis-p-methoxy compound (I) is 1.45 debye units, an average of a maximum value of 2.46 and a minimum value of 0.43 debye units. The observed dipole moments of the trans- and cis-p-methoxy compounds (I) are 2.65 (82° isomer) and 2.18 (53° isomer) debye units, respectively. The observed values are approximately 0.6-0.7 debye units higher than the calculated values, but the difference between the moments observed of the cis- and trans-p-methoxy compounds (I) is essentially that calculated. On this basis the isomer with the highest dipole moment is assigned the trans configuration. This is the same as that originally given by Stoermer and Simon [12].

Migratory Aptitudes and Reaction Mechanisms

The tendency for various groups to rearrange or migrate in the elimination rearrangement reaction of 1,1-diaryl-2-bromoethylenes is called the migratory aptitude of the groups. One reasonable approach to measuring this tendency is to examine the rates of the elimination-rearrangement reaction of various substituted phenyl groups on the vinyl bromide. However, inherent in such a study is the problem of the effect of the substituent group on the acidity of the vinyl hydrogen. In view of the known stereospecificity of this reaction, it was thought that this problem could be obviated by examining the relative rates of rearrangements of the cis and trans isomers in which only one of the phenyl rings contained the substituent under consideration. Thus, the cis and trans isomers of 1-p-methoxyphenyl-1-phenyl-2-bromoethylene (cis- and trans-I), 1-p-chlorophenyl-1-phenyl-2-bromoethylene (cis- and trans-II) and 1,1-diphenyl-2-bromoethylene (III) were prepared. In these five different compounds we have an electron-donating group ($-OCH_3$) on the migrating phenyl, an electron withdrawing group (-Cl) on the migrating phenyl and what we could call our neutral or reference group (-H). In a pair of isomers, if the trans group is migrating with its electrons the electron-donating group would be expected to increase the rate of the reaction. If, on the other hand, the phenyl is migrating without its electrons, the electron-donating group would be expected to retard the reaction whereas the electron withdrawing group would be expected to increase the rate. This study of migratory aptitudes can be compared to the known migratory aptitudes in the pinacol rearrangements.

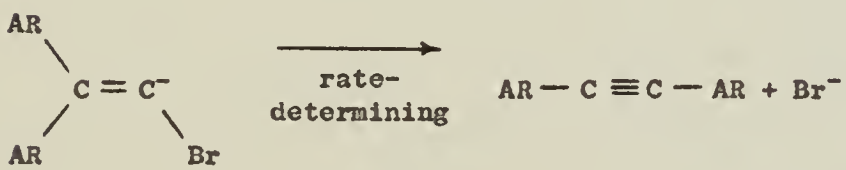


In the pinacol rearrangement it was found that the migratory aptitudes for a phenyl migrating are as follows [28]:

$$p\text{-}OCH_3 > p\text{-alkyl} > p\text{-}H > p\text{-}Cl$$

The general reaction mechanism [8,9] for the reaction of 1,1-diaryl-2-bromoethylenes with potassium-t-butoxide may be written as follows:

IV V



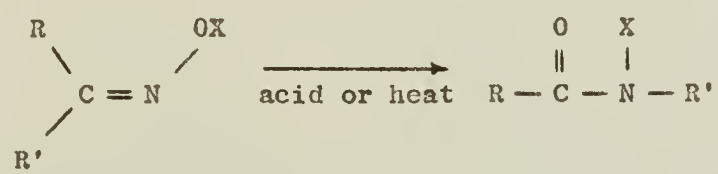
AR = aryl group

Because of the wide variety of strong bases [1-10] which can initiate the rearrangement a reasonable first step in the reaction is the abstraction of the vinyl proton to form anion V. By the use of deuterated solvent Pritchard and Bothner-By [9] have exchanged the

vinyl hydrogen of IV with a deuterium atom. They have calculated the exchange reaction to be at least a hundred times faster than the conversion to diphenylacetylene at the same temperature. Moreover, the rates for the rearrangement reactions are considerably faster in deuterated solvent than they are in t-butyl alcohol. From this information it is plausible that the reaction mechanism involves reversible carbanion (V) formation. If the formation of carbanion V were irreversible, so that its formation would be the rate-determining step, the reaction of deuterated substrate would proceed more slowly than that of undeuterated substrate (IV). Further evidence that the abstraction of a proton is not the rate-determining step, using potassium-t-butoxide as the base, is the difference in rate constants of the cis and trans isomers observed by the author. In my opinion, the cis- and trans-p-methoxy compounds (I), for example, should be identical as far as the abstraction of the vinyl proton is concerned, yet they have rate constants of 1.06 and 1.62 x 10^{-3} (min.$^{-1}$), respectively. The most reasonable explanation of these rate constants is that the migration is involved in the rate-determining step, rather than occuring after it. On the other hand, Curtin and Flynn [7] have demonstrated that in the formation of diphenylacetylene, 1,1-diphenyl-2-bromoethylene-2-d reacts at an appreciably slower rate with butyl-lithium than does 1,1-diphenyl-2-bromoethylene. This would indicate that the breaking of the carbon-hydrogen bond is the rate-determining step when butyl-lithium is used as a base. However, under these conditions, the first step of the reaction is most probably not reversible.

The second step, or rate-determining step of the reaction, using potassium-t-butoxide as the base, is the migration of the group trans to the bromine atom. Implicit in this system is the configurational stability of anion V. The fact that the trans group migrates and anion V was stable was demonstrated by Bothner-By [8] and by Curtin, et al. [10]. Bothner-By prepared the cis and trans isomers of 1-p-bromophenyl-1-phenyl-2-bromoethylene-1-^{14}C and converted them to labeled 4-bromotolans using potassium-t-butoxide in refluxing t-butyl alcohol (ca. 83°). By oxidizing the tolans, radioactive benzoic and p-bromobenzoic acids were obtained. From this he found the cis isomer to rearrange with 88 percent migration of the phenyl group while the trans isomer rearranged with 92 percent migration of the p-bromophenyl group. Curtin, et al., found similar results with cis and trans p-chloro compounds using butyl-lithium to initiate the reaction at -35°.

It might be well to point out now the similarity between this rearrangement and the Beckmann rearrangement [29]. The Beckmann rearrangement involves migration between doubly-bonded carbon and nitrogen with the migration of the group trans to the leaving -OH or -OR group.



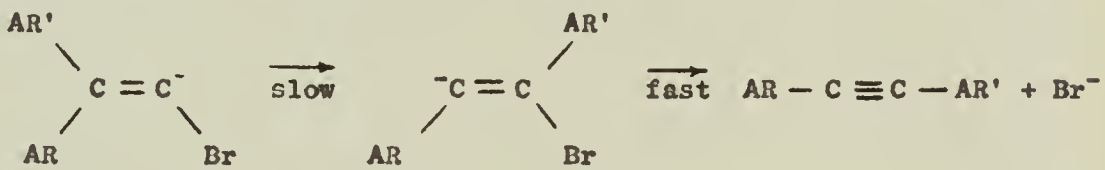
X = H or R group,

R', R = alkyl or aryl group

Moreover, the nitrogen atom is isoelectronic with carbanion V. There are, of course, differences in the reactions, the most obvious being the initial reaction with strong base in our rearrangement while the Beckmann is initiated with acids or heat.

There remains unanswered the important questions of migratory aptitudes and of the detailed reaction mechanism of the second step of our reaction. The three most reasonable mechanisms for the migration step are:

1. The slow migration of the trans aryl group without its electrons followed by a fast loss of bromide ion:

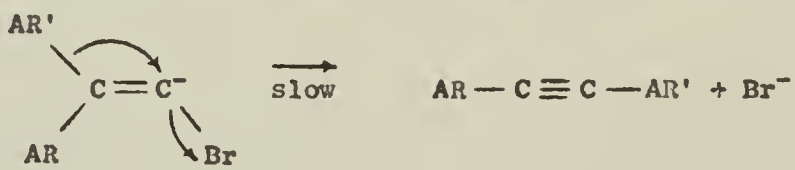


V VI

2. The same as mechanism 1 except that the first step is fast and the second slow.

It was important to consider these two mechanisms because the rearrangement of phenyl groups without their electrons to carbanions has been postulated by Zimmerman and co-workers [30].

3. The slow rearrangement of the trans group with its electron accompanied by the displacement of bromide ion.



The values of the average rate constants, a measure of migratory aptitudes in our reactions, are summarized in Table 12.

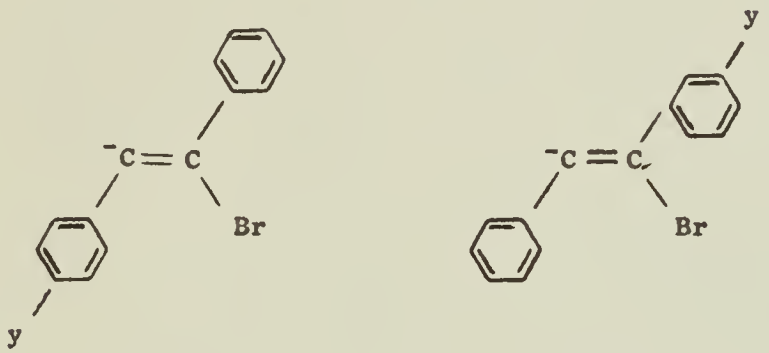
It can be seen, from a comparison of the rate constants of the cis- and trans- p-methoxy compounds (I), that the migrating group donating electrons into our system speeds up the reaction over the migrating neutral or reference group. Conversely, the cis- and trans-p-chloro compounds (II) indicate that the migrating group withdrawing electrons slows down the reaction compared to the migrating reference group. Normally, this type of information could be taken as evidence that a group is migrating with its electrons [28,29]. Thus, mechanism 1 would appear unlikely because the slow migration without electrons would predict the opposite orders. For example, Zimmerman and Zweig [30] have shown that a p-tolyl group migrates slower than a phenyl group in the rearrangement reactions of 1-chloro-2-phenyl-2-p-tolylpropane with lithium. This is consistent with an electron-donating group ($-CH_3$) retarding the rate of rearrangement compared to a phenyl group when the groups are rearranging without their electrons. Any effect of the various substituted phenyl groups on anion VI would not affect the rate of the reaction since this anion is formed after the rate-determining step. However, in mechanism 2 the stability or instability of anion VI would certainly be expected to affect the rate of the reaction since this anion is formed before the slow step of the reaction. For example, anion VI-a of the cis-p-chloro compound (II) would be expected to be more

TABLE 12

AVERAGE RATE CONSTANTS FOR THE REACTIONS OF 1-PHENYL-1-*p*-SUBSTITUTED PHENYL-2-BROMOETHYLENES WITH 0.20M POTASSIUM-*t*-BUTOXIDE

Compounds	k x 10^3(min.$^{-1}$)
trans-1-*p*-methoxyphenyl-1-phenyl-2-bromoethylene	1.62
cis-1-*p*-methosyphenyl-1-phenyl-2-bromoethylene	1.06
trans-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene	0.45
cis-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene	1.04
1,1-diphenyl-2-bromoethylene	0.82

stable than anion VI-b of the trans-p-chloro compound (II) due to the electron-withdrawing effect of the p-chloro group.

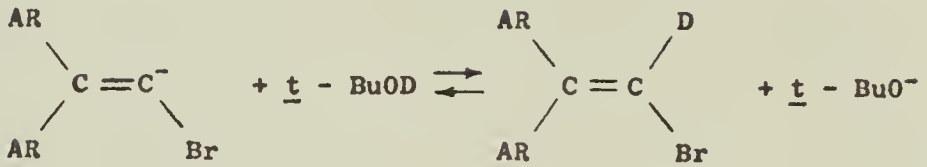


VI-a VI-b

y = -Cl or $-OCH_3$

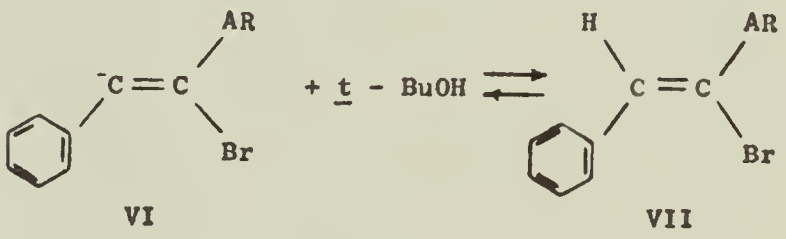
Conversely, anion VI-a of the cis-p-methoxy compound (I) would be less stable than anion VI-b of the trans-p-methoxy compound (I) due to the destabilization of the cis-I anion by the p-methoxy group. Thus, from an examination of the relative rates of reaction of the cis-trans pairs of isomers it is seen that the results can be made equally consistent with either mechanism 2 (rapid equilibration of the two anions followed by slow loss of bromide) or mechanism 3 (migration of the phenyl with its electrons). Furthermore, a more careful comparison, not only of the relative rates of the cis-trans pairs, but also of the relative rates of various compounds, leads to the same conclusions; although, admittedly, some of the assumptions required to rationalize the results with mechanism 2 are rather unlikely. However, in the discussion to follow, it is seen that mechanism 2 becomes a very unlikely possibility.

As was pointed out earlier, Bothner-By [9] succeeded in trapping anion V with deuterium.



V

It is certainly reasonable that anion VI, in which the carbanion electrons have the possibility of being conjugated with a phenyl or substituted phenyl group, would be at least as stable, and probably more stable, than anion V. Therefore, if present, anion VI or VI' should react with solvent by an analogous reaction to that of anion V to give VII, VII', or both



VI VII

VI' VII'

Possible Conjugation

A reaction of 1,1-diphenyl-2-bromoethylene (III) with potassium-t-butoxide was, therefore, allowed to proceed to partial completion and the crude mixture, after neutralization, was carefully analyzed for trans- and cis-monobromostilbene, the products of anions VI and VI'. By the use of vapor-phase chromatography, infrared spectra and a comparison with authentic samples it was shown that the reaction mixture resulting from the partial reaction of the 1,1-diphenyl olefin (III) with base consisted only of starting material and diphenylacetylene. There was no detectable trace of the bromostilbenes. These results tend to exclude mechanism 2 as being operative.

The third mechanism involves the slow rearrangement of the trans group with its electrons. The rate constants for the cis and trans isomers are consistent with this mechanism. The trans-p-methoxy compound (I) would be expected to react faster than the cis-p-methoxy compound (I) because the migrating group is p-methoxyphenyl in trans-I and phenyl in cis-I. According to mechanism 3, the p-methoxy group, being an electron-donating group, increases the rate of the rearrangement compared to the rate of rearrangement of a phenyl group. Conversely, the cis-p-chloro compound (II) reacts faster than the trans-p-chloro compound (II) because a p-chlorophenyl group is migrating in trans-II, retarding the rate of the reaction.

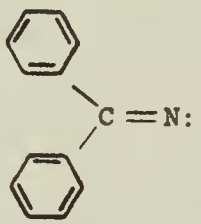
Phenyl is the migrating group in the cis-p-methoxy compound (I) and in the cis-p-chloro compound (II). The differences in rate constants between the cis isomers and 1,1-diphenyl olefin (III) is reasonably due to the effects of the stationary substituted phenyl groups.

Probably the most important of these effects is the acidity of the vinyl hydrogen abstracted in the first step of the reaction. Roberts and co-workers [31] have measured the rates of deuterium-proton exchange of o-, m-, and p-deuterated fluorobenzene, benzotrifluoride and anisole. In such reactions the combined inductive and field effects of the substituents on the benzene ring appear to be of major importance and the electromeric effects of minor importance. They have shown that fluorine, although four carbon atoms from the deuterium atom, increases the rate of the removal of deuterium two hundred times over that of the unsubstituted deuterobenzene. The methoxy group had little effect on the acidity of the deuterium atom. In view of this paper we can be fairly certain that the chlorine atom of the cis-p-chloro compound (II), having the same type of effect as the fluorine atom, would increase, at least to some degree, the acidity of the vinyl hydrogen over that of the acidity of the vinyl hydrogen of 1,1-diphenyl olefin (III). It is reasonable, therefore, to say that the cis-p-chloro compound (II) reacts faster than the 1,1-diphenyl olefin (III) due to the greater acidity of the vinyl hydrogen.

The cis-p-methoxy compound (I) also reacts faster than 1,1-diphenyl olefin (III). Since Roberts, et al., [31], have shown that the methoxy group has little effect on the acidity of the deuterium atom it is difficult to rationalize cis-I reacting faster than III. One possible explanation of this increase is the possible stabilization of the incipient carbon-carbon triple bond by the p-methoxyphenyl group. Probably occurring simultaneously with the migration of the

trans aryl group is the formation of the carbon-carbon triple bond. Since the p-methoxyphenyl group is conjugated with the vinyl group it probably has some effect on the formation of the triple bond. Depuy and Leary [32] have shown that in the pyrolytic elimination reactions of some acetates of substituted 1, 3-diphenyl-2-propanols the reaction is controlled by the stability of the olefin formed. In these cases, the olefin formed conjugated with a p-methoxy phenyl group predominated by a factor of ca. three over that of an olefin formed conjugated to a phenyl group. These results would indicate that the p-methoxyphenyl group stabilizes the incipient double bond compared to a phenyl group. The fact that the cis-p-methoxy compound (I) reacts faster than 1,1-diphenyl olefin (III) could be explained, therefore, by the greater stability of the triple bond being formed in the reaction of the cis-p-methoxy compound (I). The trans-p-methoxy compound (I) reacts faster than 1,1-diphenyl olefin (III) due to the p-methoxyphenyl group aiding in the rearrangement with electrons. Conversely, the trans-p-chloro compound (II) retards the rate of the reaction compared to 1,1-diphenyl olefin (III) because the p-chlorophenyl group destabilizes the rearrangement of the trans group with its electrons. Comparing the rate constants of the cis and trans isomers to each other is consistent with mechanism 3. In view of this and the reasonable rationalization of the relative rate constants of the cis and trans isomers to 1,1-diphenyl-2-bromoethylene, mechanism 3 is certainly the most probable.

There remains the question of just what is the driving force of the rearrangement, or why do groups rearrange with their electrons to an electron-rich site? In the Beckmann rearrangement the polarity of the N-OX bond is thought to influence the rearrangement [29]. The more powerfully the OX group attracts electrons the faster the rearrangement. This could conceivably give rise to a partial breaking of the N-OX bond, leaving a vacant orbital to which the trans group could migrate. There is no evidence that there is any actual dissociation into free ions. This would result in a nitrogen sextet intermediate sometimes postulated for the Beckmann rearrangement [33].



This intermediate is unreasonable due to the stereospecificity of the rearrangement.

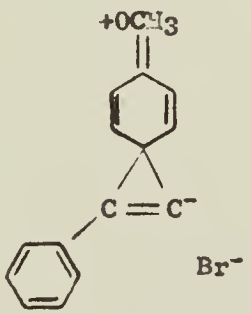
It is then conceivable that the partial breaking of the carbon-bromine bond and the probable rehybridization to give a vacant p orbital, into which the trans group could migrate, would be the driving force of the rearrangement. There are many cases of ionization of a halide resulting from the formation of a carbanion. The most common of these are the well known carbene reactions [34-36]. In particular, the reaction of chloroform with sodium hydroxide

involves an initial rapid proton transfer and then a slow loss of chloride ion from the resulting carbanion [34].

$$CHCl_3 + OH^- \rightleftharpoons {}^-CCl_3 + H_2O$$

$${}^-CCl_3 \xrightarrow{\text{slow}} :CCl_2 + Cl^-$$

The fact that the chloride ion does not ionize until the carbanion is formed might explain why the rearrangement is initiated by the removal of the vinyl proton. Once the vinyl carbanion is formed the bromide atom can ionize, at least to some degree, causing the formation of the vacant p orbital necessary for the rearrangement. An extreme case of this might be depicted as such:



This poses the problem of why, in the Beckmann rearrangement, the rate constant of the p-methoxyphenyl group migrating is so much greater than that of the phenyl group migrating, while in our rearrangement it is not? For instance, R. Huisgen and co-workers [37] have found trans-p-methoxyacetophenone oxime to react ca. 150 times faster than acetophenone oxime, yet trans-p-methoxy compound I reacts only 1.6 times as fast as cis-p-methoxy compound I. Even though the nitrogen atom in

the Beckmann rearrangement is isoelectronic with the carbanion in our rearrangement the fact remains that the nitrogen atom is neutral and the carbon has a negative charge. If the driving force of the reaction is the partial breaking of the C-Br bond, this would still leave some negative charge on the carbon atom while the partial breaking of the N-O% bond would leave the nitrogen atom partially positive. This difference in charge on the migrating terminus affecting the rates of reaction is reflected in other rearrangements where the group is migrating with its electrons. For instance, the rate constant for the migrating p-methoxyphenyl in the symmetrical pinacol rearrangement is five hundred times greater than the migrating phenyl group [28]. In this rearrangement the group is believed to migrate to a positively charged terminus. In the Lossen and Hofmann rearrangements the phenyl or substituted phenyl groups are migrating to a negatively charged nitrogen atom. Hauser, et al. [38], have indicated the migrating p-methoxyphenyl group to be ca. six times as fast as the migrating phenyl group in the Lossen rearrangement while in the Hofmann rearrangement they found it to be approximately ten times as fast. This comparison of charge on migrating terminus would tend to predict a small difference in rate between p-methoxyphenyl and phenyl due to a group migrating with its electrons to an electron-rich site.

The p-chlorophenyl group, on the other hand, does not affect the rates of rearrangement to a radical degree [28,29,39]. Chapman and Fidler [39] have shown that the picryl ether of p-chlorobenzophenone-

β-oxime reacts 1/5 as rapidly as the picryl ether of benzophenone under the same conditions. The fact that the trans-p-chloro compound (II) reacts 1/2 as rapidly as 1,1-diphenyl olefin (III) is not surprising from this comparison.

CHAPTER V

SUMMARY

A kinetic study of the migratory aptitude, or tendency of a group to rearrange, was made on the cis and trans isomers of a series of 1-phenyl-1-p-substituted phenyl-2-bromoethylenes. The kinetics of the reactions of the bromoethylenes with base was followed by measuring the ultraviolet absorption spectra of the products obtained. Rate constants for the rearrangement of the bromoethylenes showed that an electron-donating group on the migrating phenyl increases the rate of the reaction compared to a phenyl group. Conversely, an electron withdrawing group on a migrating phenyl retards the rate of the reaction. Kinetic results also indicated that the cis-bromoethylenes reacted faster than 1,1-diphenyl-2-bromoethylene.

Three mechanisms have been considered for the reactions and the most reasonable consists of a rapid equilibrium involving the reaction of the bromoethylene with base followed by a slow rearrangement of the phenyl or substituted phenyl group with its electrons.

A comparison of the elimination-rearrangement reaction to the Beckmann, Pinacol, Lossen and Hofmann rearrangements is made, and the differences between the elimination-rearrangement reaction and the others is rationalized.

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BIOGRAPHICAL SKETCH

Ralph Anthony Damico, Jr., was born in Chester, Pennsylvania, on July 2, 1935. In June, 1957, he received the degree of Bachelor of Science in Chemistry from Saint Joseph's College, Philadelphia, Pennsylvania, and enrolled in the graduate school of the University of Florida. During his graduate study at the University of Florida he has held a graduate assistantship, a teaching assistantship and a Texaco research fellowship in the Chemistry Department.

Mr. Damico is married to the former Darrina Dee Turner. He is a member of the American Chemical Society and of Gamma Sigma Epsilon fraternity.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

February 3, 1962

Dean, College of Arts and Sciences

Dean, Graduate School

Supervisory Committee:

Chairman

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